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March 24, 2017

Ms. Carolyn d'Almeida  
U.S. EPA, Region IX  
75 Hawthorne Street, SFD-8-1  
San Francisco, California 94105

**Subject: Contract No. EP-W-07-066, Task Order No 066-016-09Q1, Williams Air Force Base Task Order, Review of the Groundwater Model presented in the Final Remedial Design and Remedial Action Work Plan for Operable Unit 2, Revised Groundwater Remedy, Site ST012, May 2014, and the Draft Final Addendum #2, Remedial Design and Remedial Action Work Plan for Operable Unit 2, Revised Groundwater Remedy, Site ST012, Former Williams Air Force Base, Mesa, Arizona, March 2016**

Dear Ms. d'Almeida:

TechLaw has conducted a review of the Groundwater Model presented in the Final Remedial Design and Remedial Action Work Plan for Operable Unit 2, Revised Groundwater Remedy, Site ST012, dated May 23, 2014, and the Draft Final Addendum #2, Remedial Design and Remedial Action Work Plan for Operable Unit 2, Revised Groundwater Remedy, Site ST012, Former Williams Air Force Base, Mesa, Arizona, dated March 15, 2016.

The comments are being forwarded to you in Word format. TechLaw understands you will review and revise these comments at your discretion.

We appreciate the opportunity to provide technical support services to U.S. EPA on this Task Order. Should you have any questions or comments, please contact the TechLaw Project Manager, Michael Anderson, at (415) 762-0564.

Sincerely,

A handwritten signature in cursive script that reads 'Indira D. Balkissoon'.

Indira Balkissoon  
ROC 9 Senior Task Order Manager

DC:KB:MA:as

cc: Central files, TechLaw, Inc.

**FORMER WILLIAMS AIR FORCE BASE  
Mesa, Arizona**

**Review of the Groundwater Model presented in the  
Final Remedial Design and Remedial Action Work Plan for Operable Unit 2  
Revised Groundwater Remedy, Site ST012, May 2014  
and the  
Draft Final Addendum #2  
Remedial Design and Remedial Action Work Plan for Operable Unit 2  
Revised Groundwater Remedy, Site ST012  
March 2016**

**Submitted to:**

**Ms. Carolyn d'Almeida  
U.S. Environmental Protection Agency  
Region IX SFD-8-1  
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**Submitted by:**

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**Task Order No.  
Contract No.  
EPA TOCOR  
Telephone No.  
TechLaw TO Manager  
Telephone No.**

**066-016-09Q1  
EP-W-07-066  
Carolyn d'Almeida  
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**March 24, 2017**

**Review of the Groundwater Model presented in the Final Remedial Design and Remedial Action Work Plan for Operable Unit 2, Revised Groundwater Remedy, Site ST012 May 2014, and the Draft Final Addendum #2, Remedial Design and Remedial Action Work Plan for Operable Unit 2, Revised Groundwater Remedy, Site ST012 Former Williams Air Force Base, Mesa, Arizona, March 2016**

## **GENERAL COMMENTS**

1. The assumptions about mass transfer that were made for the Williams Groundwater Model are not consistent with recent research on mass transfer from light nonaqueous phase liquid (LNAPL) to groundwater. Mass transfer of constituents from LNAPL to groundwater at the ST012 site has been demonstrated to be rate-limited based on a detailed field mass transfer test (MTT) and related model evaluation of the data (Mobile et al., 2016; Kavanaugh et al., 2011). These findings are consistent with extensive research on NAPL dissolution rates that has been conducted over the past few decades (e.g., Miller et al., 1990). Mobile et al. (2016) also suggest that LNAPL dissolution rates will likely decrease with time as more LNAPL is removed and residual saturation (and related LNAPL globule and ganglia surface areas) decreases. The initial MTT was conducted immediately prior to the introduction of steam to the thermal enhanced extraction (TEE) test cell (Kavanaugh et al., 2011). However, the Groundwater Model assumes equilibrium conditions exist between LNAPL and aqueous-phase benzene, toluene, ethylbenzene, xylenes, and naphthalene (BTEX-N) constituents (i.e., unlimited mass transfer, resulting in effective solubility concentration levels in LNAPL areas). The Groundwater Model uses the MODFLOW SURFACT software; this equilibrium assumption is used to develop the governing transport equations and numerical solution techniques that form the basis of MODFLOW SURFACT [e.g., Section 2.2.3 (governing transport equations with residual NAPL) of the MODFLOW SURFACT User's Manual; HydroGeoLogic, 1996]. For example, SEAM3D modeling of the MTT indicates that under the observed rate-limited conditions, benzene concentrations in extraction-well effluent are likely to be as much as a factor of five or more times lower than equilibrium concentrations (Mobile et al., 2016; Figure 9). Therefore, the Groundwater Model may overestimate LNAPL dissolution rates by almost an order of magnitude and, depending on enhanced bioremediation (EBR) biodegradation rates (and whether the BTEX electron donor or the sulfate electron acceptor concentrations are limiting), may significantly underestimate remediation time frames. Please analyze the MTT results and evaluate the impacts of rate-limited LNAPL dissolution on the Groundwater Model predictions and the EBR system performance and design.
2. Groundwater Model soil-water partition coefficient input values should be corrected. The Groundwater Model was developed using BTEX-N soil-water partition coefficients,  $K_d$ , estimated from soil organic carbon measurements,  $f_{oc}$  ( $K_d = k_{oc} f_{oc}$ , where  $k_{oc}$  is the chemical-specific soil organic carbon-water partition coefficient; Lyman et al., 1982).  $K_d$  is a very important chemical transport parameter (comparable in importance to hydraulic conductivity) which is used to compute the chemical retardation factor,  $R_d$ , assuming linear equilibrium partitioning of mass between the soil (solid) and pore-water

phases (Hemond and Fechner, 1994): [ EMBED Equation.DSMT4 ]. ([ EMBED Equation.DSMT4 ] is the soil matrix bulk dry density and  $n_e$  is the effective soil porosity). For example, the chemical migration rate is directly proportional to hydraulic conductivity and inversely proportional to  $R_d$ . The total contaminant mass in an aquifer is also directly proportional to  $R_d$ , as well as aquifer cleanup times once the source is removed (e.g., Zheng et al., 1991). The  $f_{oc} - k_{oc}$  relationship is valid for  $f_{oc} > 0.001$  (Schwarzenbach and Westall, 1981; Hemond and Fechner, 1994, Section 3.5.1), but the Groundwater Model was based on  $f_{oc} = 0.0003$ . When the soil organic carbon content is low, research has shown that sorption sites other than organic carbon (e.g., adsorption of organic compounds to mineral surfaces) become increasingly important (Schwarzenbach and Westall, 1981). Due to these factors the  $f_{oc} - k_{oc}$  studies indicate that  $f_{oc}$  should not be less than 0.001 when computing  $K_d$  (Schwarzenbach and Westall, 1981). Since the Groundwater Model used  $f_{oc} = 0.0003$ , the simulated BTEX-N advection, dispersion, and biodegradation rates could all be as much as a factor of three times too high, and the Groundwater Model may significantly underestimate remediation time frames depending on the relative importance of aqueous-phase transport mechanisms (advection, dispersion, sorption, biodegradation) and LNAPL dissolution rates. Please correct the Groundwater Model soil-water partition coefficient input values and evaluate the impacts on the Groundwater Model predictions and the EBR system performance and design. Please also include in the modeling report the site-specific  $f_{oc}$  measurements from earlier investigations.

3. The sources [field measurements (e.g., from slug tests or pumping tests), model calibration, or assumption] of hydraulic conductivity (K) values for the Groundwater Model are not explained clearly in the modeling reports and the sensitivity of the EBR simulations and design to K was not evaluated. For example, the Final Remedial Design and Remedial Action Work Plan, Former Liquid Fuels Storage Area, Site ST012, Former Williams Air Force Base, Mesa, Arizona, May 2014 (RD-RAWP) Appendix E modeling report states that the Cobble Zone (CZ) was “assigned”  $K=70$  feet/day and that K of the Lower Saturated Zone (LSZ) was determined from some form of model calibration without specifying the details. However, in the Groundwater Model, K in the LSZ ranges from 10 to 12 feet/day, but the MTT measured order-of-magnitude higher depth-averaged LSZ K values of 80 to 300 feet/day (Mobile et al., 2016). The source of K values for the Upper Water Bearing Zone (UWBZ) was not clearly specified, other than stating that these K values came from earlier modeling work (e.g., BEM, 2010). Further, the Groundwater Model assumes that the vertical hydraulic conductivity,  $K_z$ , is a factor of ten lower than horizontal K, but no field measurements of  $K_z$  were made. The modeling report acknowledges that  $K_z$  is an important parameter for EBR system design (e.g., it affects vertical groundwater flow from the UWBZ to the CZ near UWBZ injection wells), and it is well-established (Hantush, 1964) that  $K_z$  is an important hydraulic parameter for designing partially-penetrating extraction/injection wells, such as those utilized in the EBR design. Please examine the sensitivity of the EBR system design (e.g., well spacing, flushing rates, sulfate loadings) and simulated remediation times to reasonable variations in horizontal and vertical hydraulic conductivity values. Please ensure that the sensitivity and uncertainty analyses take into account the number of

available K measurements for each hydrogeologic unit and discrepancies in LSZ K values suggested by the recently-published MTT results.

4. The Groundwater Model reports indicate that the EBR design is based largely on groundwater flow and pathline modeling as opposed to chemical transport (advection-dispersion), sorption, and biodegradation modeling. Full-scale reactive transport modeling was only performed to estimate remediation time frames based on predicted benzene concentrations (e.g., Table E-4.14 in Appendix E of the RD-RAWP). The modeling reports present significant discussions of groundwater and sulfate “mixing” rates and times, but it is very difficult to independently evaluate these statements and calculations in relation to how the field-scale EBR system will actually perform or whether reactive transport modeling would yield similar results. Please use the reactive transport model to demonstrate the sensitivity of the EBR design (e.g., well spacing and pumping rates) and remediation time-frame estimates to all of the key Groundwater Model input parameters, including those discussed in this set of comments.
5. Due to the Groundwater Model complexity, it is not possible to independently evaluate the predictive EBR simulations (e.g., 20-year benzene concentration predictions) because no model outputs are presented in the reports. The MODFLOW SURFACT code automatically writes output files containing the relevant simulation results, and figure generation (contour plots and x-y graphs) is straightforward using modern Graphical User Interfaces (GUIs) (e.g., Groundwater Vistas), but none of these were added to the reports. For this type of flow and transport simulation, the following standard output needs be included in the modeling report to enable independent analysis and review: horizontal and vertical groundwater (aqueous-phase) concentration contour plots (all constituents; BTEX-N and sulfate) for selected layers in each hydrogeologic unit and for several times during the simulation (including initial conditions); hydraulic head contour and velocity vector plots; LNAPL saturation contour plots for different layers and times; LNAPL constituent mole- or mass-fraction contour plots for different layers and times; and various time-dependent mass balance x-y graphs (total LNAPL volume/mass; various LNAPL constituent (e.g., BTEX-N) mass plots; total aqueous-phase mass for each constituent (BTEX-N and sulfate); total BTEX-N constituent mass sorbed to soil; and total mass (BTEX-N and sulfate) versus time into and out of the model for these sources and sinks: biodegradation (sink), BTEX-N dissolution from LNAPL, extraction/injection wells, inflow/outflow through model domain boundaries, and change in mass storage (aqueous- and sorbed-phases).
6. The Appendix E RD-RAWP modeling report does not provide justification for increasing the sulfate utilization rate. The following statements relative to biodegradation rates under sulfate-reducing conditions are made in Section 4.5.6 of the Appendix E modeling report in the RD-RAWP: *“For the purpose of this assessment; and, without in-situ tests to provide a sulfate utilization rate and/or a decrease in half saturation constants under sulfate amended conditions, the utilization rate of sulfate was increased 10 fold from that value shown in Table E-4.11 (emphasis added)”* and, *“It is assumed that sulfate reducing bacteria biomass in the presence of high concentrations of sulfate will experience exponential growth and this will increase the efficiency and utilization of sulfate for petroleum hydrocarbon biodegradation.”* The justifications for increasing the

biodegradation rate for sulfate-reducing conditions by such a large amount (10 times) do not appear to be very strong. It is unclear what evidence is available from site-specific EBR monitoring to support such a high biodegradation rate in the predictive modeling. Considering that it is very difficult to predict with high a high degree of confidence future, and spatially-varying biodegradation rates, please examine in more detail the sensitivity of the EBR design and model predictions of future benzene concentrations to a reasonable range of biodegradation rates.

7. The longitudinal dispersivity,  $\alpha_L$ , value used in the Groundwater Model for the LSZ ( $\alpha_L = 10$  feet) is much larger than the  $\alpha_L$  measured during the MTT (LSZ value of  $\alpha_L = 2$  feet; Mobile et al., 2016). Appendix C, Section 3.3, in the Draft Final Addendum #2, Remedial Design and Remedial Action Work Plan for Operable Unit 2, Revised Groundwater Remedy, Site ST012, Former Williams Air Force Base, Mesa, Arizona, March 2016 (Addendum #2) recommends that future modeling use  $\alpha_L = 20$  feet based on the results of the EBR field push/pull test. Addendum #2 also recommends that future EBR transport modeling increase the horizontal and vertical transverse dispersivities by about a factor of ten. A critical review of dispersivity observations from 59 different field sites (Gelhar et al., 1992) indicates that the LSZ value of  $\alpha_L = 2$  feet would be more appropriate for a site of this scale. Since dispersion is an important mixing mechanism, please examine the sensitivity of the EBR design and model predictions to the dispersivity parameters (longitudinal, transverse horizontal, and transverse vertical).
8. Slow desorption of contaminants from the soil matrix and larger-scale aquifer heterogeneities has been well-established as an important field-scale mechanism that reduces the effectiveness of remediation systems (e.g., the “tailing effect” in pump-and-treat effluent concentration reductions; Hadley and Newell, 2012, 2014; Siegel, 2014; Sudicky and Illman, 2011; Culver et al., 1997), but this was not considered in the Groundwater Model. Multi-rate desorption can also significantly impact effluent concentrations for extraction and monitoring wells (Cosler, 2004). Slow desorption of aqueous-phase constituents, in addition to rate-limited LNAPL dissolution, should also realistically be expected to have some level of impact on the EBR system performance (e.g., extend remediation time frames). The RD-RAWP modeling report frequently acknowledges the importance of heterogeneities but does not present any quantitative analyses of their potential effects. Please include analyses of the potential impacts of aquifer heterogeneities (e.g., hydraulic conductivity, soil-water partition coefficient, and biodegradation rate) on EBR performance.

## REFERENCES

- BEM, 2010. *Technical Evaluation Report of Phase I TEE Pilot Test Performance Evaluation Report*.
- Cosler, D.J. 2004. Effects of Rate-Limited Mass Transfer on Water Sampling with Partially Penetrating Wells. *Ground Water*, Vol. 42, no. 2. pp. 203-222.

- Culver, T.B., S.P. Hallisey, D. Sahoo, J.J. Deitsch, and J.A. Smith. 1997. Modeling the Desorption of Organic Contaminants from Long-Term Contaminated Soil Using Distributed Mass Transfer Rates. *Environmental Science and Technology*, 31(6), 1581-1588.
- Gelhar, L.W., C. Welty, and K.R. Rehfeldt. 1992. A Critical Review of Data on Field-Scale Dispersion in Aquifers. *Water Resources Research*. Vol. 28, No. 7. pp. 1955-1974.
- Hadley, P.W., and C.J. Newell. 2012. Groundwater Remediation: The Next 30 Years. *Groundwater*, Vol. 50, No. 5. 669-678.
- Hadley, P.W., and C.J. Newell. 2014. The New Potential for Understanding Groundwater Contaminant Transport. *Groundwater*, Vol. 52, No. 2. 174-186.
- Hantush, M.S. 1964. Hydraulics of Wells. *Advances in Hydroscience*. Vol. 1. Academic Press. Ed. V.T. Chow. 282-437.
- Hemond, H.F., and E.J. Fechner. 1994. *Chemical Fate and Transport in the Environment*. Academic Press.
- HydroGeoLogic, 1996. MODFLOW-SURFACT Software (version 3.0) Documentation, Volume II: Transport Modules.
- Kavanaugh, M.C., R. Deeb, J. Nyman, L. Stewart, and M. Widdowson. 2011. Improved Field Evaluation of NAPL Dissolution and Source Longevity. ESTCP, Arlington, VA.
- Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1982. *Handbook of Chemical Property Estimation Methods*. McGraw-Hill Book Company.
- Miller, C.T., M.M. Poirier-McNeill, and A.S. Mayer. 1990 Dissolution of Trapped Nonaqueous Phase Liquids: Mass-Transfer Characteristics. *Water Resources Research*, 26(11), pp. 2783-2796.
- Mobile, M., M. Widdowson, L. Stewart, J. Nyman, R. Deeb, M. Kavanaugh, J. Mercer, and D. Gallagher. 2016. In-Situ Determination of Field-Scale NAPL Mass Transfer Coefficients: Performance, Simulation and Analysis. *Journal of Contaminant Hydrology*, 187, pp. 31-46.
- Siegel, D.I. 2014. On the Effectiveness of Remediating Groundwater Contamination: Waiting for the *Black Swan*. *Groundwater*, Vol. 52, No. 4. 488-490.
- Schwarzenbach, R.P., and J. Westall. 1981. Transport of Nonpolar Organic Compounds from Surface Water to Groundwater. Laboratory Sorption Studies. *Environmental Science & Technology*, 15(11), pp. 1360-1367.
- Sudicky, E.A., and W.A. Illman. 2011. Lessons Learned from a Suite of CFB Borden Experiments. *Groundwater*, Vol. 49, No. 5. 630-648.

Zheng, C., G.D. Bennett, and C.B. Andrews. 1991. Analysis of Ground-Water Remedial Alternatives at a Superfund Site. *Groundwater*, Vol. 29, No. 6. 838-848.